

# PATENT ABSTRACTS OF JAPAN

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(30)Priority

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## (54) INK JET PRINTING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an ink jet printing method for improving the water resistance fastness of an ink jet image formed of water based ink containing an anionic dye.

SOLUTION: The ink jet printing method is to improve the water resistance fastness of an ink jet image, in which an ink jet printing method comprises the steps of preparing an ink jet recording element containing a carrier having an image recording layer containing a cross-linking polymer of gelatin or acetoacetylated polyvinyl alcohol and a mordant, and adapting like an image liquid ink droplets of an anionic water soluble dye, and also causing a polymer to be cross-linked by immersing the element in a solution of a hardening agent.

## LEGAL STATUS

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**CLAIMS**

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[Claim(s)]

[Claim 1] The ink-jet printing approach including preparing the ink-jet record element which comes to contain the base material which has the image-recording layer which is the ink-jet printing approach for raising the waterproof fastness of an ink-jet image, and contains the cross-linking polymer and the mordant of a aceto acetylation polyvinyl alcohol, image Mr. applying the liquid liquid-ink drop of anionic water soluble dye to the b aforementioned image-recording layer, and dipping the c aforementioned element into the water solution of a hardening agent in a list, and making said polymer construct a bridge.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the ink jet printing approach for raising the waterproof fastness of the ink jet image formed from the water color ink containing an anionic color.

[0002]

[Description of the Prior Art] Ink jet printing is a method of drawing the non-impact type by answering a digital signal and making a liquid ink drop adhere to an image recording element for every pixel. The approach of using for controlling adhesion of a liquid ink drop to an image recording element, and producing a desired image is various. Electrify the continuous flow of a drop and it is made to image Mr. deviate on the front face of an image recording element by a certain approach learned as a continuous system ink jet, and the drop by which image formation is not carried out to coincidence is captured, and it returns to an ink reservoir. Each liquid ink drop is discharged if needed on an image recording element, and a desired image is made to form in the option known as a drop on-demand type ink jet. A piezoelectric transducer and thermal bubble formation are included in the general approach of controlling discharge of a liquid ink drop in drop on-demand type printing. There is an extensive application to some parts of the commercial scene covering the range from label pasting on industry to short-time printing for a desk document and pictures image formation in an ink jet printer.

[0003] The ink used in various ink jet printers can be classified into either a color system or a pigment system. A color is distribution or a coloring agent by which a solvation is carried out in molecule by the dispersion medium. In a room temperature, a dispersion medium may be a liquid or may be a solid-state. The dispersion medium generally used is the mixture of water or water, and an organic auxiliary solvent. Each color molecule of each is surrounded with the molecule of a dispersion medium. In color system ink, a particle cannot observe at all under a microscope. Although there were many advances in the technique of color system ink jet ink recently, it still has a fault, like such ink is deficient in color fastness to light with the usually low optical density in the paper. When using water as a dispersion medium, as for such ink, it is common to also have the fault that waterproof fastness is scarce.

[0004] JP,10-219,157,A is related with the ink jet ink which comes to contain the very little glutaraldehyde as an aquosity medium, a coloring agent, and a destruction-of-life agent.

[0005] When it prints on an image recording element, there is a problem in use of the ink in the specification of JP,10-219,157,A in that the waterproof fastness of the obtained image is scarce.

[0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention is offering the ink jet printing approach for raising the waterproof fastness of the ink jet image formed from the water color ink containing an anionic color. Another purpose of this invention is offering the ink jet printing approach which raises the waterproof fastness of an ink jet image with the application of a hardening agent. Another purpose of this invention is offering the ink jet printing approach which non-image Mr. applies a hardening agent to the whole element.

[0007]

[Means for Solving the Problem] According to this invention, it is the ink jet printing approach for

raising the waterproof fastness of an ink jet image. a) The ink jet record element which comes to contain the base material which has an image recording layer containing the cross-linking polymer and mordant of aceto acetylation polyvinyl alcohol is prepared, b) — image Mr. applying the liquid liquid ink drop of anionic water soluble dye to the image recording layer concerned, and a list — c — the ink jet printing approach including dipping the element concerned into the water solution of a hardening agent, and making the polymer concerned construct a bridge is offered.

[0008] It was found out that the waterproof fastness of an image improves by processing by this hardening agent solution.

[0009] According to this approach, since a hardening agent is applicable to both an image formation field and a non-image formation field, the advantage in which it excels introducing a hardening agent into ink is offered.

[0010]

[Embodiment of the Invention] If the cross-linking polymer used is made to construct a bridge, which hardening agent can also be used for this invention. A hardening agent may be preferably used by 0.10 – 5.0 mass [ of the active principle in a water solution ] %, and the concentration covering the range of 0.25 – 2.0 mass %.

[0011] When wished, the hardening agent water solution may contain other components generally added in an auxiliary solvent, a wetting agent, a surface active agent, and ink jet ink.

[0012] The example of the hardening agent which can be used for this invention is classified into the class from which following many differ (those mixture is included).

[0013] a) The compound containing two or more aldehyde functional groups, such as homologous series of the dialdehyde covering the range which attains to an AJIPO aldehyde from a glyoxal at a formaldehyde list, (a succinic acid aldehyde and glutaraldehyde, a diethylene glycol aldehyde, aromatic series dialdehyde, etc. are included).

[0014] b) BUROKKUTO hardening agents (matter usually guided from the activity hardening agent which emits an activity compound under suitable conditions) (for example, a tetrahydro-4-hydroxy-5-methyl-2(1H)-pyrimidinone polymer —), such as matter containing a block tor RUDEHIDO functional group 1 anhydrous glucose unit : The polymer of the type which has the glyoxal polyol resultant which consists of 2 glyoxal units, JIMETOKI sill ethanal-melamine non-formaldehyde resins, 2, 3-dihydroxy – 1,4-dioxane, As various aliphatic series in BUROKKUTO dialdehyde and a list as formaldehyde or cyclic amide, a urea, and N-methylol compound obtained from condensation with nitrogen heterocycle.

[0015] c) olefin association activated by the adjoining electron withdrawing group and the activity olefin compound (for example, a divinyl ketone —) which especially has two or more non-permuted vinyl groups Resorcinol screw (vinyl sulfonate) 4, 6-screw (vinyl sulfonyl) – meta xylene, Screw (vinyl sulfonyl alkyl) The ether and an amine, 1 and 3, 5-tris (vinyl sulfonyl) Hexahydro –s-triazine, A JIAKURIRU amide, 1, 3-screw (acryloyl) Urea, N, and N'-bismaleimide, Bis-iso maleimide, screw (2-acetoxy ethyl) A ketone, 1 and 3, 5-thoria chestnut roil hexahydro –s-tolidine, a list — screw (2-acetoxy ethyl) A ketone and 3, 8-dioxo decane –1, and 10-screw (perchloric acid pyridinium) Screw (vinyl sulfonylmethane) Screw (vinyl sulfonyl methyl ether) etc. — BUROKKUTO activity olefin of a type.

[0016] d) The compound containing two or more amino groups (for example, ethylenediamine). It is

[0017] to a list. e) Mineral salt (they are salts, such as a titanium dioxide and a zirconium dioxide, to chromium salt, such as potassium alum of an aluminum sulfate and aluminum and ammonium alum, an ammonium-carbonate zirconium, a chromium sulfate, and chromium alum, and a list).

[0018] The following are contained in the example of a hardening agent useful to this invention.

Hardening-agent 1: Aluminum-sulfate hardening agent 2: Screw (vinyl sulfonylmethane) (Eastman Kodak Company)

A hardening agent 3:2, 3-dihydroxy – 1,4-dioxane (Aldrich Chemical Co.)

Hardening-agent 4: Ethylenediamine hardening-agent 5:glyoxal hardening agent 6: Screw (vinyl sulfonyl methyl ether) (Eastman Kodak Company)

Hardening-agent 7: Glutaraldehyde hardening-agent 8:1 anhydrous glucose unit: The glyoxal polyol resultant which consists of 2 glyoxal units, and SQUAREZ(trademark) 755 (Sequa Chemicals, Inc.)

Hardening-agent 9:1 annular urea unit: The annular urea glyoxal condensation product which

consists of 1 glyoxal unit, and SUNREZ(trademark)700M Hardening agent (Sequa Chemicals, Inc.) 10:JIMETOKI sill ethanal-melamine non-formaldehyde resins and Sequa CPD 3086-100 (Sequa Chemicals, Inc.)

[0019] In a desirable mode, the image recording layer used for the approach of this invention may contain hardening agents, such as what is enumerated above for use in a water solution, again. this voice — the hardening agent which can be set like, and 0.008 – 0.2 g/m<sup>2</sup> — desirable — 0.02 – 0.09 g/m<sup>2</sup> You may use in an amount.

[0020] Which anionic water soluble dye, such as a color which has an anionic radical (for example, a sulfonic group or a carboxylic-acid radical), may be used for this invention. An anionic color is COLOR INDEX. Although you may be any of the acid dye currently enumerated, direct dye, or reactive dye, it is not limited to these. Metalization and nonmetal-ized azo dye may be used as indicated in the U.S. Pat. No. 5,482,545 specification. Other colors which may be used are the Europe patent public presentation official report No. 802246 and publication number. It is found out by each specification of 09 No. -202043 official report. In a desirable mode, the anionic water soluble dye which may be used for this invention is metalization azo dye, nonmetal-ized azo dye, xanthene dye, METARO phthalocyanine dye, or sulfur dye. The mixture of these colors may be used. color and 0.1 to 10 mass % — the amount of 0.25 – 3 mass % may exist preferably.

[0021] If the result of a request called fixing of an anionic color is produced, which mordant can also be used for this invention. the [ for example, / a cationic polymer (for example macromolecule quaternary ammonium compound) or a basic polymer (for example, the condensation product of polymethacrylic acid (dimethylaminoethyl), polyalkylene polyamine, and them and dicyano diamine, an amine-epichlorohydrin polycondensation object), and / divalent ] — II group metal ion, lecithin, and a phospholipid compound may be used. The following mordants are used in the desirable mode of this invention.

[0022] Mordant 1: Vinylbenzyl trimethylammonium chloride / 2 methacrylic-acid ethylene glycol (Eastman Kodak Company) Mordant 2: Pori (vinylbenzyl trimethylammonium chloride) SP2 707 (SP2 Company)

Mordant 3: Pori (2- N, N, and N-trimethylammonium) Ethyl meta-KURIRETOMETO sulfate (Eastman Kodak Company) Mordant 4: Pori (3- N, N, and N-trimethylammonium) Propyl methacrylate chloride, Polycare (trademark) (Rhône-Poulenc Co.)

Mordant 5: Pori (diaryl dimethylammonium chloride) (Aldrich Chemical Co.) Mordant 6: Cationic polyethylene polyamine resin and Niccajet(trademark) 117 (Nicca-USA)

Mordant 7: An amine and a glycidyl polymer, and Niccajet(trademark) 450 (Nicca-USA)

Mordant 8: (3- N, N, and N-trimethylammonium) The hydroxyethyl cellulose by which reforming (derivitize) was carried out by propyl chloride, and Celquat(trademark) SC-240C (National Starch Co.)

Mordant 9: An alumina covering colloid silica and Ludox(trademark) CL (DuPont)

Mordant 10: A ratio is the copolymer of the vinylbenzyl trimethylammonium chloride of 50:30:20, butyl acrylate, and screw-vinylbenzene. (Eastman Kodak Company) [0023] The mordant used for this invention may be used in which an amount effective in the purpose planned. Generally, it is an element. 0.5 – 5 g/m<sup>2</sup> A good result is obtained when the mordant of an amount exists.

[0024] Aceto acetylation polyvinyl alcohol useful to this invention is indicated by for example, the U.S. Pat. No. 4,350,788 specification. These ingredients are Nippon. It is marketed as Gohsefimer (trademark) Z-200 from Gohsei.

[0025] The purpose which the image recording layer used for the approach of this invention contributes to the property of not blocking again sake, and the flattening agent (for example, a titanium dioxide —) for controlling the dirt-proof nature Giant-molecule beads, such as a bead of a zinc oxide, a silica and a bridge formation polymethyl methacrylate, or polystyrene, A surface active agent (for example, cationic surface active agents, such as a nonionic hydrocarbon, a fluorocarbon surface active agent, or quaternary ammonium salt), Various known additives containing a fluorochrome, a pH regulator, a defoaming agent, lubricant, antiseptics, a viscosity controlling agent, a color fixing agent, a waterproofing agent, a dispersant, an ultraviolet ray absorbent, an antifungal agent, a mordant, an antistatic agent, an antioxidant, a fluorescent brightener, etc. can also be contained.

[0026] The ink jet ink used for the approach of this invention is common knowledge in the

technical field concerned. The ink constituent used for ink jet printing is a liquid constituent which comes to contain a solvent or a carrier liquid, a color, a wetting agent, an organic solvent, a detergent, a thickener, antiseptics, a conductive enhancement agent, a Kogation inhibitor, a drying agent, a defoaming agent, etc. generally. A solvent or a carrier liquid can also be used as the water which could also consider as mere water or was mixed with other water miscibility solvents, such as polyhydric alcohol. Organic materials, such as polyhydric alcohol, may use the ink which is a main carrier or a solvent liquid. Especially a useful thing is the mixed solvent of water and polyhydric alcohol.

[0027] A carrier can exist in ink jet ink and ink can change with the descriptions of the ink jet printer made into the purpose extensively. It is a dispersion medium with the mixture of water or water, and a miscibility organic auxiliary solvent desirable to the printer which uses water color ink. Ink hardens by drying, it helps to prevent adding an auxiliary solvent (zero to 20 mass [ of ink ] %), and solidifying in the orifice of a print head, or ink helps to permeate acceptor material. In the desirable auxiliary solvent for the ink used for this invention, they are glycerol, ethylene glycol, propylene glycol, and 2-methyl. Those mixture is contained in -2, 4-pentanediol and a diethylene glycol, and a list, and the concentration as the whole is crossed to the range of 5 - 20 mass % of ink.

[0028] The base material for the ink jet record element used for this invention Paper, resin coat paper, polyethylene terephthalate, polyethylenenaphthalate, and a microporosity ingredient (for example, PPG Industries of Pittsburgh and Pennsylvania and the polyethylene polymer content ingredient currently sold by Inc. by the trade name of Teslin (trademark) — Tyvek (trademark) synthetic paper (DuPont Corp.) And OPPalyte (trademark) film (MobilChemical Co.) Other complex films currently enumerated by the list at the U.S. Pat. No. 5,244,861 specification, It can also be made any although usually used for an ink jet acceptor.

[0029] The base material used for this invention has the thickness of 75 to 300 micrometer preferably 50 to 500 micrometer. When wished, an antioxidant, an antistatic agent, a plasticizer, and other known additives may be introduced into the base material concerned. Paper is used in a desirable mode.

[0030] In order to improve the adhesive property to the base material of an image recording layer, before applying an image recording layer, the front face of a base material may be given to corona discharge treatment.

[0031] Furthermore, under coats, such as a layer formed from a halogenation phenol or the vinyl chloride-vinyl acetate copolymer hydrolyzed partially, can be applied on the surface of a base material, and the adhesive property of an image recording layer can also be raised. When using an under coat, the thickness (namely, desiccation coating thickness) should be less than 2 micrometers.

[0032] Which amount with an image recording layer effective in the purpose planned may exist. Generally, a good result is obtained when the image recording layer of the amount of 8 - 15 g/m<sup>2</sup> (5-30 micrometers is preferably equivalent to the dry thickness of 8-15 micrometers) exists preferably, 5 - 30 g/m<sup>2</sup> and.

[0033]

[Example] The following examples are offered in order to explain this invention.

[0034] The polyethylene resin coat paper of photograph grade is given to corona discharge treatment, next it is 7.7 g/m<sup>2</sup>. Gohsefimer(trademark) Z-200 (Nippon Gohsei) 0.9 g/m<sup>2</sup> It applied in the image formation layer with a mordant 1. Some of these coatings were made to also contain the hardening agent 5 of an amount currently enumerated in Table I. The air-drying of these coatings was applied and carried out using the extrusion hopper.

[0035] Hewlett-Packard containing an anionic cyanogen color Ink jet cartridge (H.P. 51649A) It obtained. The ink of this cyanogen is Direct Blue 199. And AcidBlue 9 Mixture was contained (mass ratio 6:1). This ink is indicated by the U.S. Pat. No. 5,536,306 specification.

[0036] next, Hewlett-Packard a printer (H.P.690C) and the above-mentioned cartridge are used — the patch of cyanogen was printed on the acceptor by 100% of lei down.

[0037] Unless all the acceptance elements except a reference were refused especially, it dipped in the bath containing the hardening agent solution which comes to contain 1% solution of the hardening agent shown in Table I, and the air dried was carried out all night.

[0038] Next, these elements were dipped in distilled water for 1 hour, and then carried out the air dried all night. Optical density before and after dipping in water was measured using the X-Rite (trademark) concentration meter. Waterproof fastness is measured as a percentage of the optical density which remains after being immersed to water. The value nearest to 100% is desirable. The value exceeding 100% shows "dot expansion" which is not desirable. The following results were obtained.

[0039]

[Table 1]

表 1

コーティング中の硬膜剤 5 (質量%)	浴中の硬膜剤	水試験後の残存光学濃度 (%)
無 し	無し (対照標準)	8
(0.25)	" ( " )	172
(0.50)	" ( " )	161
(0.75)	" ( " )	163
無 し	1	73
(0.25)	1	93
(0.50)	1	97
(0.75)	1	101
無 し	2	80
(0.25)	2	107
(0.50)	2	91
(0.75)	2	97
無 し	3	97
(0.25)	3	93
(0.50)	3	107
(0.75)	3	98
無 し	4	92
(0.25)	4	96
(0.50)	4	97
(0.75)	4	97
無 し	5	101
(0.25)	5	97
(0.50)	5	95
(0.75)	5	98
無 し	無し (対照標準)	179
(0.25)	5 (0.25)	99
(0.25)	5 (0.50)	98
(0.25)	5 (1)	109
(0.25)	5 (2)	110
(0.25)	5 (3)	101

[0040] It is shown that the above-mentioned data have the waterproof fastness (number nearest to 100%) which was excellent as compared with the reference element which the ink jet image obtained by this invention did not dip into the hardening agent solution. Any amelioration was not offered, either, when there was no hardening agent during a bath, although it was also when a result was improved, even if it included the hardening agent during coating.

[0041]

[Effect of the Invention] It was found out that the waterproof fastness of an image improves by processing by this hardening agent solution. According to this approach, since a hardening agent is applicable to both an image formation field and a non-image formation field, the advantage in which it excels introducing a hardening agent into ink is offered.

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the ink jet printing approach for raising the waterproof fastness of the ink jet image formed from the water color ink containing an anionic color.

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**PRIOR ART**

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[Description of the Prior Art] Ink jet printing is a method of drawing the non-impact type by answering a digital signal and making a liquid ink drop adhere to an image recording element for every pixel. The approach of using for controlling adhesion of a liquid ink drop to an image recording element, and producing a desired image is various. Electrify the continuous flow of a drop and it is made to image Mr. deviate on the front face of an image recording element by a certain approach learned as a continuous system ink jet, and the drop by which image formation is not carried out to coincidence is captured, and it returns to an ink reservoir. Each liquid ink drop is discharged if needed on an image recording element, and a desired image is made to form in the option known as a drop on-demand type ink jet. A piezoelectric transducer and thermal bubble formation are included in the general approach of controlling discharge of a liquid ink drop in drop on-demand type printing. There is an extensive application to some parts of the commercial scene covering the range from label pasting on industry to short-time printing for a desk document and pictures image formation in an ink jet printer.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] It was found out that the waterproof fastness of an image improves by processing by this hardening agent solution. According to this approach, since a hardening agent is applicable to both an image formation field and a non-image formation field, the advantage in which it excels introducing a hardening agent into ink is offered.

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] The purpose of this invention is offering the ink jet printing approach for raising the waterproof fastness of the ink jet image formed from the water color ink containing an anionic color. Another purpose of this invention is offering the ink jet printing approach which raises the waterproof fastness of an ink jet image with the application of a hardening agent. Another purpose of this invention is offering the ink jet printing approach which non-image Mr. applies a hardening agent to the whole element.

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## MEANS

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[Means for Solving the Problem] According to this invention, it is the ink jet printing approach for raising the waterproof fastness of an ink jet image. a) The ink jet record element which comes to contain the base material which has an image recording layer containing the cross-linking polymer and mordant of aceto acetylation polyvinyl alcohol is prepared, b) — image Mr. applying the liquid ink drop of anionic water soluble dye to the image recording layer concerned, and a list — c — the ink jet printing approach including dipping the element concerned into the water solution of a hardening agent, and making the polymer concerned construct a bridge is offered.

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[0009] According to this approach, since a hardening agent is applicable to both an image formation field and a non-image formation field, the advantage in which it excels introducing a hardening agent into ink is offered.

[0010]

[Embodiment of the Invention] If the cross-linking polymer used is made to construct a bridge, which hardening agent can also be used for this invention. A hardening agent may be preferably used by 0.10 – 5.0 mass [ of the active principle in a water solution ] %, and the concentration covering the range of 0.25 – 2.0 mass %.

[0011] When wished, the hardening agent water solution may contain other components generally added in an auxiliary solvent, a wetting agent, a surface active agent, and ink jet ink.

[0012] The example of the hardening agent which can be used for this invention is classified into the class from which following many differ (those mixture is included).

[0013] a) The compound containing two or more aldehyde functional groups, such as homologous series of the dialdehyde covering the range which attains to an AJIPO aldehyde from a glyoxal at a formaldehyde list, (a succinic acid aldehyde and glutaraldehyde, a diethylene glycol aldehyde, aromatic series dialdehyde, etc. are included).

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[0015] c) olefin association activated by the adjoining electron withdrawing group and the activity olefin compound (for example, a divinyl ketone —) which especially has two or more non-permuted vinyl groups Resorcinol screw (vinyl sulfonate) 4, 6-screw (vinyl sulfonyl) – meta xylene, Screw (vinyl sulfonyl alkyl) The ether and an amine, 1 and 3, 5-tris (vinyl sulfonyl) Hexahydro –s-triazine, A JIAKURIRU amide, 1, 3-screw (acryloyl) Urea, N, and N'-bismaleimide, Bis-iso maleimide, screw (2-acetoxy ethyl) A ketone, 1 and 3, 5-thoria chestnut roil hexahydro –s-tolidine, a list — screw (2-acetoxy ethyl) A ketone and 3, 8-dioxo decane –1, and 10-screw (perchloric acid pyridinium) Screw (vinyl sulfonylmethane) Screw (vinyl sulfonyl methyl ether) etc. — BUROKKUTO activity olefin of a type.

[0016] d) The compound containing two or more amino groups (for example, ethylenediamine). It is [0017] to a list. e) Mineral salt (they are salts, such as a titanium dioxide and a zirconium dioxide, to chromium salt, such as potassium alum of an aluminum sulfate and aluminum and ammonium alum, an ammonium-carbonate zirconium, a chromium sulfate, and chromium alum, and a list).

[0018] The following are contained in the example of a hardening agent useful to this invention. Hardening-agent 1: Aluminum-sulfate hardening agent 2: Screw (vinyl sulfonylmethane) (Eastman Kodak Company)

A hardening agent 3:2, 3-dihydroxy - 1,4-dioxane (Aldrich Chemical Co.)

Hardening-agent 4: Ethylenediamine hardening-agent 5:glyoxal hardening agent 6: Screw (vinyl sulfonyl methyl ether) (Eastman Kodak Company)

Hardening-agent 7: Glutaraldehyde hardening-agent 8:1 anhydrous glucose unit: The glyoxal polyol resultant which consists of 2 glyoxal units, and SQUAREZ(trademark) 755 (Sequa Chemicals, Inc.)

Hardening-agent 9:1 annular urea unit: The annular urea glyoxal condensation product which consists of 1 glyoxal unit, and SUNREZ(trademark)700M Hardening agent (Sequa Chemicals, Inc.) 10:JIMETOKI sill ethanal-melamine non-formaldehyde resins and Sequa CPD 3086-100 (Sequa Chemicals, Inc.)

[0019] In a desirable mode, the image recording layer used for the approach of this invention may contain hardening agents, such as what is enumerated above for use in a water solution, again. this voice — the hardening agent which can be set like, and 0.008 - 0.2 g/m<sup>2</sup> — desirable — 0.02 - 0.09 g/m<sup>2</sup> You may use in an amount.

[0020] Which anionic water soluble dye, such as a color which has an anionic radical (for example, a sulfonic group or a carboxylic-acid radical), may be used for this invention. An anionic color is COLOR INDEX. Although you may be any of the acid dye currently enumerated, direct dye, or reactive dye, it is not limited to these. Metalization and nonmetal-ized azo dye may be used as indicated in the U.S. Pat. No. 5,482,545 specification. Other colors which may be used are the Europe patent public presentation official report No. 802246 and publication number. It is found out by each specification of 09 No. -202043 official report. In a desirable mode, the anionic water soluble dye which may be used for this invention is metalization azo dye, nonmetal-ized azo dye, xanthene dye, METARO phthalocyanine dye, or sulfur dye. The mixture of these colors may be used. color and 0.1 to 10 mass % — the amount of 0.25 - 3 mass % may exist preferably.

[0021] If the result of a request called fixing of an anionic color is produced, which mordant can also be used for this invention. the [ for example, / a cationic polymer (for example macromolecule quaternary ammonium compound) or a basic polymer (for example, the condensation product of polymethacrylic acid (dimethylaminoethyl), polyalkylene polyamine, and them and dicyano diamine, an amine-epichlorohydrin polycondensation object), and / divalent ] — II group metal ion, lecithin, and a phospholipid compound may be used. The following mordants are used in the desirable mode of this invention.

[0022] Mordant 1: Vinylbenzyl trimethylammonium chloride / 2 methacrylic-acid ethylene glycol (Eastman Kodak Company) Mordant 2: Pori (vinylbenzyl trimethylammonium chloride) SP2 707 (SP2 Company)

Mordant 3: Pori (2- N, N, and N-trimethylammonium) Ethyl meta-KURIRETOMETO sulfate (Eastman Kodak Company) Mordant 4: Pori (3- N, N, and N-trimethylammonium) Propyl methacrylate chloride, Polycare (trademark) (Rhône-Poulenc Co.)

Mordant 5: Pori (diaryl dimethylammonium chloride) (Aldrich Chemical Co.) Mordant 6: Cationic polyethylene polyamine resin and Niccajet(trademark) 117 (Nicca-USA)

Mordant 7: An amine and a glycidyl polymer, and Niccajet(trademark) 450 (Nicca-USA)

Mordant 8: (3- N, N, and N-trimethylammonium) The hydroxyethyl cellulose by which reforming (derivitize) was carried out by propyl chloride, and Celquat(trademark) SC-240C (National Starch Co.)

Mordant 9: An alumina covering colloid silica and Ludox(trademark) CL (DuPont)

Mordant 10: A ratio is the copolymer of the vinylbenzyl trimethylammonium chloride of 50:30:20, butyl acrylate, and screw-vinylbenzene. (Eastman Kodak Company) [0023] The mordant used for this invention may be used in which an amount effective in the purpose planned. Generally, it is an element. 0.5 - 5 g/m<sup>2</sup> A good result is obtained when the mordant of an amount exists.

[0024] Aceto acetylation polyvinyl alcohol useful to this invention is indicated by for example, the U.S. Pat. No. 4,350,788 specification. These ingredients are Nippon. Gohsei to Gohsefimer (trademark) Z-200 It is marketed by carrying out.

[0025] The purpose which the image recording layer used for the approach of this invention contributes to the property of not blocking again sake, and the flattening agent (for example, a titanium dioxide —) for controlling the dirt-proof nature Giant-molecule beads, such as a bead of a zinc oxide, a silica and a bridge formation polymethyl methacrylate, or polystyrene, A surface active agent (for example, cationic surface active agents, such as a nonionic hydrocarbon, a fluorocarbon surface active agent, or quaternary ammonium salt), Various known additives containing a fluorochrome, a pH regulator, a defoaming agent, lubricant, antiseptics, a viscosity controlling agent, a color fixing agent, a waterproofing agent, a dispersant, an ultraviolet ray absorbent, an antifungal agent, a mordant, an antistatic agent, an antioxidant, a fluorescent brightener, etc. can also be contained.

[0026] The ink jet ink used for the approach of this invention is common knowledge in the technical field concerned. The ink constituent used for ink jet printing is a liquid constituent which comes to contain a solvent or a carrier liquid, a color, a wetting agent, an organic solvent, a detergent, a thickener, antiseptics, a conductive enhancement agent, a Kogation inhibitor, a drying agent, a defoaming agent, etc. generally. A solvent or a carrier liquid can also be used as the water which could also consider as mere water or was mixed with other water miscibility solvents, such as polyhydric alcohol. Organic materials, such as polyhydric alcohol, may use the ink which is a main carrier or a solvent liquid. Especially a useful thing is the mixed solvent of water and polyhydric alcohol.

[0027] A carrier can exist in ink jet ink and ink can change with the descriptions of the ink jet printer made into the purpose extensively. It is a dispersion medium with the mixture of water or water, and a miscibility organic auxiliary solvent desirable to the printer which uses water color ink. Ink hardens by drying, it helps to prevent adding an auxiliary solvent (zero to 20 mass [ of ink ] %), and solidifying in the orifice of a print head, or ink helps to permeate acceptor material. In the desirable auxiliary solvent for the ink used for this invention, they are glycerol, ethylene glycol, propylene glycol, and 2-methyl. Those mixture is contained in -2, 4-pentanediol and a diethylene glycol, and a list, and the concentration as the whole is crossed to the range of 5 - 20 mass % of ink.

[0028] The base material for the ink jet record element used for this invention Paper, resin coat paper, polyethylene terephthalate, polyethylenenaphthalate, and a microporosity ingredient (for example, PPG Industries of Pittsburgh and Pennsylvania and the polyethylene polymer content ingredient currently sold by Inc. by the trade name of Teslin (trademark) —) Tyvek (trademark) synthetic paper (DuPont Corp.) And OPPalyte (trademark) film (MobilChemical Co.) Other complex films currently enumerated by the list at the U.S. Pat. No. 5,244,861 specification, It can also be made any although usually used for an ink jet acceptor.

[0029] The base material used for this invention has the thickness of 75 to 300 micrometer preferably 50 to 500 micrometer. When wished, an antioxidant, an antistatic agent, a plasticizer, and other known additives may be introduced into the base material concerned. Paper is used in a desirable mode.

[0030] In order to improve the adhesive property to the base material of an image recording layer, before applying an image recording layer, the front face of a base material may be given to corona discharge treatment.

[0031] Furthermore, under coats, such as a layer formed from a halogenation phenol or the vinyl chloride-vinyl acetate copolymer hydrolyzed partially, can be applied on the surface of a base material, and the adhesive property of an image recording layer can also be raised. When using an under coat, the thickness (namely, desiccation coating thickness) should be less than 2 micrometers.

[0032] Which amount with an image recording layer effective in the purpose planned may exist. Generally, a good result is obtained when the image recording layer of the amount of 8 - 15 g/m<sup>2</sup> (5-30 micrometers is preferably equivalent to the dry thickness of 8-15 micrometers) exists preferably, 5 - 30 g/m<sup>2</sup> and.

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[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
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**EXAMPLE**

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[Example] The following examples are offered in order to explain this invention.

[0034] The polyethylene resin coat paper of photograph grade is given to corona discharge treatment, next it is 7.7 g/m<sup>2</sup>. Gohsefimer (trademark) Z-200 (Nippon Gohsei) 0.9 g/m<sup>2</sup> It applied in the image formation layer with a mordant 1. Some of these coatings were made to also contain the hardening agent 5 of an amount currently enumerated in Table I. The air-drying of these coatings was applied and carried out using the extrusion hopper.

[0035] Hewlett-Packard containing an anionic cyanogen color Ink jet cartridge (H.P. 51649A) It obtained. The ink of this cyanogen is Direct Blue 199. And AcidBlue 9 Mixture was contained (mass ratio 6:1). This ink is indicated by the U.S. Pat. No. 5,536,306 specification.

[0036] next, Hewlett-Packard a printer (H.P.690C) and the above-mentioned cartridge are used — the patch of cyanogen was printed on the acceptor by 100% of lei down.

[0037] Unless all the acceptance elements except a reference were refused especially, it dipped in the bath containing the hardening agent solution which comes to contain 1% solution of the hardening agent shown in Table I, and the air dried was carried out all night.

[0038] Next, these elements were dipped in distilled water for 1 hour, and then carried out the air dried all night. Optical density before and after dipping in water was measured using the X-Rite (trademark) concentration meter. Waterproof fastness is measured as a percentage of the optical density which remains after being immersed to water. The value nearest to 100% is desirable. The value exceeding 100% shows "dot expansion" which is not desirable. The following results were obtained.

[0039]

[Table 1]



表 1

コーティング中の硬膜剤 5 (質量%)	浴中の硬膜剤	水試験後の残存光学濃度 (%)
無 し	無し (対照標準)	8
(0.25)	" ( " )	172
(0.50)	" ( " )	161
(0.75)	" ( " )	163
無 し	1	73
(0.25)	1	93
(0.50)	1	97
(0.75)	1	101
無 し	2	80
(0.25)	2	107
(0.50)	2	91
(0.75)	2	97
無 し	3	97
(0.25)	3	93
(0.50)	3	107
(0.75)	3	98
無 し	4	92
(0.25)	4	96
(0.50)	4	97
(0.75)	4	97
無 し	5	101
(0.25)	5	97
(0.50)	5	95
(0.75)	5	98
無 し	無し (対照標準)	179
(0.25)	5 (0.25)	99
(0.25)	5 (0.50)	98
(0.25)	5 (1)	109
(0.25)	5 (2)	110
(0.25)	5 (3)	101

[0040] It is shown that the above-mentioned data have the waterproof fastness (number nearest to 100%) which was excellent as compared with the reference element which the ink jet image obtained by this invention did not dip into the hardening agent solution. Any amelioration was not offered, either, when there was no hardening agent during a bath, although it was also when a result was improved, even if it included the hardening agent during coating.

[Translation done.]